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EP 1 143 023 A1

**EUROPEAN PATENT APPLICATION** (12)

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(71) Applicant: Nippon Steel Corporation a season charet

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dissolve in a seed by werting heat and disoppeer in case or large or ultra-large heat Input wolding having an extremely The present invention relates to a steel for a long retention time a stign total perature of 1,400 °C or higher welded structure, with excellent HAZ, toughness scontinued out to be dear the excellent HAZ, toughness scontinued out to be dear the excellent of the contract of the excellent taining, in terms of wt%, C: 0.01-to 0.2%, Si: 0.02 tocal signs 800 - 20

0.5%, Mn: 0.3,to, 2%, P; 0.03% or less, S; 0.0001, to, Inelleave to latent to the a gricultural to bed and a second 0.03%, Al: 0.0005 to 0.05%, Ti; 0.003 to 0.05%, Mg; goilous and sit 0.0001 to 0.01% and 0: 0.0001 to 0.008%, with the balance consisting of Fe and unavoidable impurities; and having particles dispersed in the steel at an average particle interval of 30 to 100 µm, the particles being formed by precipitating either any one of sulfides and nitrides

singly or the both thereof in combination using Mg.con solidua ites? tained oxides with the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle sizes of 0.2 to 5 µm as aldsed size in the particle size in the size in the particle size in the particle size in the particle s their nuclei, or particles dispersed in the steel at an ay enuose color of a color of the color ing formed by precipitating either any one of sulfides and als of one as a minimized singly or the both the reof in combination usings and no seek of the seek of Mg contained oxides with the particle sizes of 0.005 to or ever the of occurs

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#### Description

#### Technical Field

[0001] The present invention relates to a steel, for a welded structure, used for an offshore structure, a line pipe for transporting natural gas or crude oil, in architecture, in shipbuilding, for a bridge, for construction equipment or the like, and a method for producing the same. More specifically, the present invention relates to a steel, for a welded structure, requiring toughness at a weld zone, having a small prior austenite grain size at a weld heat-affected zone (hereunder referred to as "HAZ") even when the steel is welded on a heat input condition that the heat input during welding widely ranges from 0.5 kJ/mm to over 150 kJ/mm, and being excellent in toughness at the weld heat-affected zone (hereunder referred to as "HAZ toughness") without depending on the heat input condition.

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#### Background Art

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[0002] From the viewpoint of preventing the brittle fracture of a welded structure such as an offshore structure or the like, studies for suppressing brittle fracture arising at a weld zone, namely, many studies related to enhancing the HAZ toughness of a used steel plate, have been reported. In recent years, for improving welding procedure efficiency, ultralarge heat input welding (20 to 150 kJ/mm) having larger weld heat input than the formerly employed large heat input welding (about 20 kJ/mm or less) has been increasingly employed.

[0003] The difference between the influence of large heat input welding on a steel plate and that of ultra-large heat input welding on a steel plate is caused by the difference of their retention times at high temperatures of 1,400°C or more (00) That is, since a retention time is extremely long in case of ultra-large heat input welding, the area where a crystal grain size markedly coarsens expands at a HAZ and toughness deteriorates considerably.

[0005] Generally, as measures for preventing the coarsening of crystal grains at a HAZ of a steel plate, known are proposed to the effect of pipping (a pipping effect) prior austenite grains (hereunder referred to as "prior").

the means to make use of the effect of pinning (a pinning effect) prior austenite grains (hereunder referred to as "prior γ grains," and the size thereof being referred to as a "prior γ grain size") by inclusion particles finely dispersed in the steel, the inclusion particles being for example. TiN described in Japanese Unexamined Patent Publication No. S55-26164 or ZrN in "a steel for a large heat input welded structure characterized by containing, in weight %, 0.01 to 0.2% of C, 0.002 to 1.5% of Si, 0.5 to 2.5% of Mn, 0.002 to 0.1% of Ti and/or Zr, 0.004% or less of Ca and/or Mg, 0.001 to 0.1% of Ce and/or La, 0.005 to 0.1% of Al and 0.002 to 0.015% of N" as described in Japanese Unexamined Patent

Publication No. S52-17314.

[0006] However, though such nitrides contribute to fining crystal grains by showing a pinning effect of pinning prior,  $\gamma$  grains without dissolving in case of small or medium heat input welding, there is a problem that the nitrides easily dissolve in a steel by welding heat and disappear in case of large or ultra-large heat input welding having an extremely long retention time at a high temperature of 1,400 °C or higher.

[0007] In the meantime, in recent years, disclosed have been the technologies of using oxides generated in molten steel for the purpose of further improving HAZ toughness. For example, Japanese Unexamined Patent Publication No. 559-190313 discloses a method for producing a steel material excellent in weldability, characterized by deoxidizing molten steel with Ti or Ti alloy and then adding Al, Mg, etc. This production method is a technology to make use of the effect of increasing a ferrite ratio by making Ti oxides act as transformation nuclei of ferrite and to attempt to improve HAZ toughness by a method different from the former method of utilizing a pinning effect by precipitates such as nitrides:

[0008] After that, in this technical field, various inventions, including the inventions of attempting to increase the number of oxides acting as intragranular transformation nuclei, have been disclosed in Japanese Unexamined Patent and Publication Nos. S61-79745, H5-43977 and H6-37364.

[0009] In particular, as described in Japanese Unexamined Patent Publication No. 559-190313 the essence of those and the like as technologies is "to evenly and finely disperse Ti containing exides usable for the formation of ferrite nuclei during y to a transformation, namely, the fining of a ferrite structure," and not to secure a pinning effect by hitrides and the like as elevention described above, but to attempt to suppress the formation of a coarse brittle structure by accelerating ferrite transformation arising in a cooling process and to attain the fining of a structure. These toughness improvement methods are all based on the technology to disperse and utilize relatively.

[0010] These toughness improvement methods are all based on the technology to disperse and utilize relatively a course structure for promoting ferrite transformation in grains. The large oxides of about 1 µm as transformation nuclei in a coarse structure for promoting ferrite transformation in grains. The large oxides of about 1 µm as transformation nuclei in a coarse structure for promoting ferrite transformation in grains. The large oxides of a low in grains of the large oxides of the structures of the large oxides of the increase in the chemical composition of the high strength steels. In this case, the existing HAZ toughness improvement measures to utilize ferrite transformation have been losing their effectiveness because of the increase of hard-one billips at a HAZ.

[0012] From the above viewpoints, to radically improve HAZ toughness, the pinning effect on prior  $\gamma$  grains can be expected on wide-ranging heat input conditions, and oxide particles can be soluble at a high temperature, like finely

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dispersed nitrides in a steel. Moreover, in this case, it is considered that, if it is possible to obtain a transformation
    capability better than existing ferrite transformation nuclei, the HAZ toughness of a steel material used in this technical
    field will improve greatly a siditocoase ton accomplicat SAF and a
                                                                                                                                                                                                                                                                                                                                                                                                              The same the second of the sec
    [0013] As a method to introduce oxides, there is a method to add a deoxidizing element such as Ti, etc. alone in a
    refining process of steel. However, in many cases, the aggregations of oxides are formed during the holding of molten or start to the holding 
    steel, resulting in the formation of coarse oxides, and the cleanliness of the steel rather deteriorates and thus toughness
    also deteriorates. To cope with that, as explained above, various contrivances for fining those oxides including a a companion
    complex deoxidizing method, have been implemented.

[0014] However, by the methods presently known, it is impossible to disperse, in steel, fine oxides having a function of gribnous.
    or simultaneously after coming out a west deutwind as a constant of any adding St and Mn at a stesimalong process; o
    Disclosure of the Invention
                                                                                                                                                                                                                                             daying the steel after further adding Males there is used to the constant or the steel after further adding Males the town the constant of the
    [0015] The object of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness of the present invention is to provide a steel for a welded structure.
    even if the steel is welded on any heat input condition, including ultra-large heat input, by improving the existing complex
    deoxidizing method, dispersing oxides and/or nitrides more finely and evenly than before, and further imposing, in
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                10925
    addition, a ferrite transformation capability on the finely dispersed particles.
   [0016] The gist of the present invention is as follows:
   [0017] (1) A steel for a welded structure with HAZ toughness not susceptible to heat input, characterized by con-
    taining, in terms of wt%,
                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               Best Mode for Carrying Out the invention
                             C: 0.01 to 0.2%.
                          Si: 0.02 to 0.5% ibiroob phorts also groups voltages and the second of t
                                                                                                                                                                                                                                                                                                                                                                                                                                                               [0024] It is known that Mq is an eighnor to orbit to
                            Mn: 0.3 to 2%,
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                            Mg: 0.0001 to 0.01%, and
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                          of the as a strong dooxidizer, had the 1890, of 1000.0 :O
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  with the balance consisting of Fe and unavoidable impurities; and having particles dispersed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm, the particles being formed in the steel at an average particle interval of 30 to 100 µm.
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  oxides with the particle sizes of 0.2 to 5 µm as their nuclei, or particles dispersed in the steel at an average particle
  interval of 30 µm or less, the particles being formed by precipitating either any one of sulfides and nitrides singly or
 the both thereof in combination using Mg contained exides with the particle sizes of 0.005 to less than 0.2 um as their sa [3200]
 nuclei.

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(2) A steel for a welded structure with HAZ toughness not susceptible to heat input according to the item (1), more diffuse.
  characterized by further containing, in terms of wt%, one or more of
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or (2), characterized by further containing, in terms of wt%, one or more of a sit to the left of a substance of the second of t
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                                                   (4) A steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of 100000
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the items (1) to (3), characterized by having the prior austenite grain sizes of 10 to 200 µm in its HAZ structure without depending on weld heat input. See the particle of the second of the control of the second of the sec

[0021] (5) A method for producing a steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of the items (1) to (4), characterized by: casting the steel in the state of adjusting the dissolved oxygen amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and a required amount of Mg successively or simultaneously after carrying out a weak deoxidation treatment by adding Si and Mn in a steelmaking process; or a de ligitação casting the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less.

[0022] (6) A method for producing a steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of the items (1) to (4), characterized by: casting the steel in the state of adjusting the dissolved oxygen amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and required amounts of Al, Ca and Mg successively or simultaneously after carrying out a weak deoxidation treatment by adding Si and Mn at a steelmaking process; or casting the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less.

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Brief Description of the Drawings

#### [0023]

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Figure 1 is a graph showing prior γ grain sizes at HAZs when the amounts of weld heat input are varied. (At 25) Figure 2 is a schematic showing the forms of complex particles having ultra-fine Mg oxides as their nuclei and their nuclei a हिंद विषय कि देशकों से उसके हैं।

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Best Mode for Carrying Out the Invention

[0024] It is known that Mg is an element to enhance the cleanliness of a steel by acting as a strong deoxidizer and \$20.0 mg. Mai 0.3 to 275. a desulfurizing agent and thus to improve HAZ toughness.

[0025] Further, as a means to improve HAZ toughness by controlling the dispersion of oxides, a technology of complex addition wherein Mg is added after Ti is added is disclosed in Japanese Unexamined Patent Publication No.

[0026] However, as quoted before, the object of the technology is to accelerate a finely dispersion of the increase Mc. 0.0707 19 3 37 8 76 of Ti oxides, which are intragranular transformation nuclei, by adding Mg for pinning the oxides.

[0027] The present inventors, paying their attention to the function of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer, had the idea that a control of Mg as a strong deoxidizer of Mg fine dispersion of oxides might be expected if the sequence and amount of the addition of the deoxidizer in a Ti added steel were controlled in a steelmaking process by making use of the characteristic of Mg which is more hardly caused and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen aggregation and coarsening than All my Out of the outcome cruhen agreement a [0028] The present invention will hereunder be explained in detail.

[0029] The present inventors systematically investigated the state of oxides when Mg was added to molten steel deoxidized weakly by adding Ti.

[0030] As a result, it was found that oxides having two kinds of particle sizes were formed either when Ti and Mg were added in the order of Ti and then Mg or when Ti and Mg were added simultaneously and further, in the state of equilibrium, Mg was added again, after the molten steel was deoxidized by Si and Mn.

[0031] Moreover, it was confirmed in the present invention that, in the first step Mg deoxidation, the same trends as stated above were also obtained when AI and Ca were added simultaneously or precedently.

[0032] One kind is Mg containing oxides having grain sizes of 0.2 to 5.0 µm and the other kind is ultra-fine MgO or 10.0 11.0 Mg containing oxides having grain sizes of 0.005 to 0.1 μm. It is thought that these oxides are formed based on the 10.0 HM On 0.02 to 1.5% following reasons.

[0033] Firstly, oxides, at the µm level composed of Ti or those mainly composed of Ti are once formed by the addition 10.0 (a). of Ti or the simultaneous addition of Ti and a small amount of Mg. Secondly, when Mg, which has strong deoxidizing in the simultaneous addition of Ti and a small amount of Mg. Secondly, when Mg, which has strong deoxidizing in the simultaneous addition of the simultaneous addi ability, is further added in this state, the oxides already formed are reduced by Mg and Mg containing oxides at the juri 2r 0.000 to 0.05 a level, mainly composed of Mg, are formed finally.

[0034] Further, in this case, in spite of the amount of dissolved oxygen lowering, new fine oxides at the sub-jum level of the amount of dissolved oxygen lowering. composed of Mg only are formed at the same time since the deoxidizing ability of Mg is stronger than that of Ti.

[0035] As a result, an increase in the particle number and the fining of the particle size, which have not been obtained by a conventional adding method, can be realized.

[0036] With regard to oxides having a size at the µm level, in general, the larger the number of oxides, having a size of 5 µm or more, is, the more the oxides tend to become the origins of fractures and, therefore, the upper limit of the Mg addition amount is regarded to be 30 to 50 ppm when Mg is added, as described in Japanese Unexamined Patent Publication No. H9-157787.

[0037] However, in the present invention, the above problem can be avoided and Mg can be added up to 100 ppm. [0038] On the other hand, in case of the deoxidation by Ti or the deoxidation by Ti and a small amount of Mg, dissolved

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oxygen still remains in the molten steel because the deoxidation is caused by a weak deoxidizing element or a small and the control of the co amount of a strong deoxidizing element. Therefore, when Mg is added again at that time, the oxidation reaction of Mg with not only the above-mentioned oxides at the µm level or sub-µm level but also the still remaining dissolved oxygen proceeds moderately and ultra-fine oxides form further. The reason why the ultra-fine oxides form is presumably that the clustering is suppressed due to the equation of the dissolved oxygen distribution in molten steel in addition to the reduction of the dissolved oxygen amount: A 1914 one of the content of the dissolved oxygen amount: A 1914 one of the content of the dissolved oxygen amount: A 1914 one of the content of the dissolved oxygen amount: A 1914 one of the content of the dissolved oxygen amount: A 1914 one of the content of the content of the dissolved oxygen amount: A 1914 one of the content of the c during casting, cooling thereafter or reheating in hot rolling processes and a security and a security and the security and t using an electron microscope, the states of the oxides existing in the steel can be arranged as described in items 1) = 1/12 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1/25 | 1 and 2) below. Here, to observe the state of oxides existing in steel, it is preferable to observe 10 visual fields or more at a specified magnification (for example, about 100,000 times in case of ultra-fine oxides) and to measure the average as a second of the contract of the con โมโลมี 🧷 This andweithor the ultra-fine oxides of พีกู ลฮา มาการ การ การ การ เกิดีสร ผิดปากใหน่ออ อูกผยใต้โลโอ prolerantially survin barraso secretar, i stristo estante de control.

1) Particles, which are formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle size of 0.2 to 5 µm as nuclei, are contained in steel at an average particle interval of 30 to 100 µm.

2) Particles, which are formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle size of 0.005 to less than 0.2 µm as nuclei, are contained sits find by the particle size of 0.005 to less than 0.2 µm as nuclei, are contained as the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to the particle size of 0.005 to less than 0.2 µm as nuclei, are contained to 0.005 to less than 0.2 µm as nuclei, are contained to 0.005 to less than 0.2 µm as nuclei, are contained to 0.005 to less than 0.2 µm as nuclei, are contained to 0.005 to less than 0.005 µm as nuclei, are contained to 0.005 particle size of 0.005 p in steel at a presenting of the present invention the second of the present invention th [0041] The present invention relates to a steel material with excellent HAZ toughness obtained by the oxides existing in the state of the above items 1) and/or 2), and provides an epoch-making technology capable of extremely suppressing in the state of the above items 1) and/or 2), and provides an epoch-making technology capable of extremely suppressing the state of the above items 1) and/or 2), and provides an epoch-making technology capable of extremely suppressing the state of the above items 1) and/or 2). the toughness change at a HAZ, which largely depended on a honor brown and the toughness change at a HAZ, which largely depended on the triput amount of the content to the content of th [0042] The improvement of HAZ toughness will further be explained hereunder.

[0043] As has been known so far, the higher the number of oxides is, and the more the sulfides and nitrides precipitate. on the oxides, the more the intragranular transformation is accelerated. Since, as shown in the above item 1), the เพอในโทย พทยา number of the particles increases over ten times compared with a conventional case and, with regard to complex (C926) Non precipitation too, 100 percent of suifides or nitrides precipitate in combination, so far as it is confirmed, Mg contained suifides or nitrides precipitate in combination too, 100 percent of suifides or nitrides precipitate in combination too in the suifice of nitrides precipitate in combination too in the suifice of nitrides precipitate in combination to face the suifice of nitrides precipitate in the suifice of nitrides precipitate in the suifice of nitrides precipitate in combination to face the suifice of nitrides precipitate in the suifice of nitrides precipitate precipitation too, 100 percent of sulfides of this description is a sulfide of the present of the present invention have an extremely large intragranular transformation ability.

oxides according to the present invention have an extremely large intragranular transformation ability.

The present invention will be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will hereunder be a segment of the present invention will here and the present invention explained based on Figure 1 is a graph obtained by measuring the prior y particle sizes at HAZs on each condition (1 kJ/mm, 10 kJ/mm, 100 kJ/mm along the axis of the abscissas still edit bine neptyre to introduce an appropriate processing the processing edition of actual joints, the prior y particle size is obtained by taking the photographs (5 pictures or more), at the prior y particle size is obtained by taking the photographs (5 pictures or more), at the prior y particle size is obtained by taking the photographs (5 pictures or more), at the prior y particle size is obtained by taking the photographs (5 pictures or more), at the prior y particle size is obtained by taking the photographs (1 lo not in a size is obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a magnification of 50 to 200 times with an optical microscope, of microscope of Mig again. by measuring the size by the cutting method. The prior  $\gamma$  particle sizes in the cases of 1 to 50 kJ/mm shown in Figure [33.00] 1 are the ones obtained by this method. [0047] On the other hand, in case of ultra-large heat input, usually, the prior particle size is obtained by calculating it as the prior γ particle including grain boundary ferrite since the grain boundary ferrite forms along the prior γ grain boundary, or by measuring the prior γ particle size from the microstructure obtained by being heated on a prescribed condition and then rapid-cooled using a reproduction thermal cycling test machine adjusted so that the heat input equivalent amounts are identical. The prior  $\gamma$  particle sizes in the cases of 100 and 150 kJ/mm shown in Figure 1 are the ones obtained from the microstructure formed by using the reproduction thermal cycling test machine, which measuring method is the latter one. [0048] In the figure, the examples of measuring an Al deoxidized steel, a Ti added Al deoxidized steel and Mg de-[0048] In the figure, the examples of measuring an Al deoxidized steel, a 11 added Al deoxidized steel and my unique oxidized steels are shown and it is understood that the susceptibility of the prior y particle size to heat input is largely industry. varied depending on the presence of Mg oxides described in the above item 2). varied depending on the presence of Mg oxides described in the above item 2).

[0049] That is, except the Mg deoxidized steels, the prior γ particle sizes become remarkably and obviously large as the heat input amount increases. the heat input amount increases.

[0050] On the other hand, it is understood that, in case that the oxides exist in the state as specified in the above items 1) and 2) or that the oxides exist in the state as specified in the above item 2), the prior y particle sizes vary extremely little in Mg deoxidized steels even though the heat input amounts are largely changed. [0051] In particular, the state of the oxides as specified in the above item 2) is a factor governing the fining of the prior y particle size prior γ particle size.

[0052] However, if a heat input amount is up to about 60 kJ/mm, the fining of the prior γ particle size can be attained.

even if the oxides exist only in the state as specified in the above item 1) (alone). [0053] Moreover, even in the state of the oxides as specified in the above item 1), a pinning force functions, though the effect is small, and when the state of the oxides as specified in the above item 2) coexists therewith, the fining of the prior  $\gamma$  particle is markedly accelerated. [0054] As a result of observing the steel plates having fine prior  $\gamma$  particles with an electron microscope, it is clarified. that there exist abundantly the MIIMIII<sub>2</sub>O<sub>4</sub> particles (MII: Mg, Ca, Fe, Mn, etc., MIII: Al, Ti, Cr, Mn, V, etc.) of a spinel type structure, having MgO and Mg of a face centered cubic structure in the size of 0.1 µm or less as the main constituent elements, or the complex particles of Mg contained oxides and sulfides and/or nitrides (TIN, etc.) as schematically n coming the livers of the shown in Figure 2. [0055] In addition, by examining the relation of crystallographic orientation between the particles of Mg contained oxides and sulfides or nitrides under the observation by an electron microscope, it is also clarified that any of the particles has the relation of a completely parallel orientation. [0056] This shows that the ultra-fine oxides of Mg act as the sites where sulfides and nitrides precipitate preferentially. That is, it is thought that the number of the nitrides effective in the pinning of crystal grains increases caused by the abundant existence of the preferential precipitation sites. [0057] In other words, it is considered that, when heat input is small, those complex particles function as the particles effectuating pinning, and, when a retention time at a high temperature is long as in ultra-large heat input welding, though nitride particles dissolve, in the present invention, many MgO or Mg contained oxides exist and, even though the nitride particles dissolve, still existing fine oxide particles function as pinning particles at a high temperature. [0058] Therefore, according to the present invention, the suppression of the prior  $\gamma$  particle growth at a HAZ, which CO. has never been obtained in a conventional steel, can be attained. [0059] Namely, one of the features of the present invention is, in addition to the remarkable improvement in intragranular transformation ability, to create the precipitation nuclei of nitrides by introducing oxides such as MgO, etc. finely in steel, which is dissimilar to the conventional case where the pinning of crystal grains by making use of hitrides such as TiN, etc. is intended, thereby to realize the increase of the number of nitrides, and, in case of small neat input welding where nitrides effectively function, to obtain the prior γ particles with the size of 10 to 200 μm at a HAZ due to the existence of those complex particles. [0060] Moreover, another feature of the present invention is that, even in large of ultra-large heat input welding where nitrides dissolve and the effect of improving toughness is never obtained formerly, the prior  $\gamma$  particle size scarcely changes at a HAZ due to the effect of oxides alone on suppressing grain growth. [0061] The method of adding Mg according to the present invention is, as described before, a method to add Si and Mn firstly, thereafter, either to adjust the oxygen amount in molten steel by adding Ti beforehand and thereafter to add the fallows a small amount of Mg little by little, or to add Ti and a small amount of Mg simultaneously and thereafter to finally add

Mg again. [0062] Though the optimum addition amount of Mg depends on the amount of oxygen and the like existing in molten steel after the addition of TI, according to an experiment, since the oxygen concentration at that time depends on the addition amount of TI and the time until Mg is added, in conclusion, no other means are required than to control the addition amounts of TI and Mg in appropriate ranges.

[0063] Further, the final optimum amount of dissolved oxygen when Mg is added is about 0.1 to 50 ppm. The lower limit of 0.1 ppm is the lower and the property of t limit of 0.1 ppm is the lowest amount of dissolved oxygen capable of forming fine Mg oxides. On the other hand, if the dissolved oxygen exceeds 50 ppm, coarse Mg oxides form and the pinning force weakens, and for that reason, the upper limit is set at 50 ppm. upper limit is set at 50 ppm. upper limit is set at 50 ppm.

[0064] With regard to the raw material of Mg used for Mg addition and its adding method, as a result of attempting a method to add metallic Mg covered by Fe folls, a method to add Mg alloys and the like, it is clarified that, with the former method, oxidation reaction is intense when the metallic Mg is supplied in molten steel and thus the yield deteriorates. For that reason, it is preferable to add Mg alloys having relatively large specific gravity when motien steel is riorates. For that reason, it is preferable to add Mg alloys having relatively large specific gravity when motien steel is not companied by the control of the control o refined under the normal atmospheric pressure. [0065] Hereafter explained will be the reasons why the chemical composition of the object steel is defined in the present invention. present invention. [0066] C is a basic element for enhancing the strength of a base steel. An addition amount of 0.01% or more is required for securing the enhancement effect. But, if it is excessively added in excess of 0.2%, weldability and toughness. of a steel deteriorate, and therefore the upper limit is set at 0.2%. [0067] Si is an indispensable element used as a deoxidizing element in steelmaking and an addition of 0.02% or more into a steel is required. However, if it is added in excess of 0.5%, HAZ toughness deteriorates, and therefore the upper limit is set at 0.5%.

[0068] Mn is an indispensable element for securing the strength and toughness of a base steel. However, if it is Lizaq e cina added in excess of 2%, HAZ toughness deteriorates markedly, but in contrast, with the addition of less than 0.3%, the strength of a base steel is hardly secured. Therefore, the addition amount is limited in the range of 0.3 to 2%.

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[0069]. P is an element affecting the toughness of a steel. Since the toughness of not only a base steel but also a good part HAZ deteriorates greatly with a content exceeding 0.03%, the upper limit is set at 0.03%; that set at 0.03%; the upper limit is set at 0.03%; that set at 0.03%; the upper limit is set at 0.03%; the [0070] S forms coarse sulfides and thus deteriorates toughness if it is added in excess of 0.03%, but, with a content one in a sulfides and thus deteriorates toughness if it is added in excess of 0.03%, but, with a content of less than 0,0001%, the amount of formed sulfides such as MnS, etc., which are effective in the generation of intragranular ferrite, lowers greatly. Therefore, the range of the addition amount is set at 0.0001 to 0.03%. notice and one make 19.1 [0071] Alis usually added as a deoxidizing agent. In the present invention, the upper limit of Alis set at 0.05% since its addition in excess of 0.05% hinders the effect of Mg addition, and its lower limit is set at 0.0005% since Al addition Ekarcotes of at least 0.0005% is required for forming MIIMIII2O4 stably. [0072] Ti is an element effective in the fining of crystal grains, acting as a deoxidizing agent and further an element to form nitrides. However, a large, amount of its addition causes the considerable deterioration of toughness due to the formation of carbides and therefore the upper limit has to be 0.05%. Then, since the addition amount of at least 0.003% ton of below is required for securing a desired effect, the range of the addition amount is set at 0.003 to 0.05% to 1, and their blew listing out think [0073] Mg is a main alloying element in the present invention and is added as a deoxidizing agent mainly. However, and we have if it is added in excess of 0.01%, coarse oxides tend to form and the toughness of a base steel and a HAZ deteriorates. Villidites as less than the same of a base steel and a HAZ deteriorates. On the other hand, with the addition amount of less than 0.0001%, the formation of exides which are required for intragranular transformation and as pinning particles cannot be sufficiently expected. Therefore, the range of the administration and as pinning particles cannot be sufficiently expected. Therefore, the range of the administration and as pinning particles cannot be sufficiently expected. Therefore, the range of the administration are also as a sufficient of the contract of the co cases of small near input (1.7 kJ/mm) and ultra-large hear tree; 150 kJ/mm), that is, [tough/0[0.0,01,000.0], that is, [tough/0[0.0,01,000.0], that is, [tough/0[0.0,01,000.0]] input very [1.7], in griging young negy to hear tree to be input very [1.7]. steel is less than 0.0001%, the number of oxides is insufficient, and therefore the lower limit is set at 0.0001%. On the history senter other hand, if the amount of remaining oxygen exceeds 0.008%, coarse oxides increase and the toughness of a base null [6600] steel and a HAZ deteriorates, and therefore the upper limit is set at 0.008%; in a cooperant noncellers discussed and a description of the present invention, one or more elements of Cu, Ni, Cr, Mo, V, Nb, Zr, Ta and B may be added as the elements which enhance strength and toughness. [0076] Cu is an effective element in enhancing strength without deteriorating toughness. However, with the amount of less than 0.05%, the effect does not appear, but, with the amount exceeding 1.5%, cracks tend to occur during the heating of a slab or welding. Therefore, the range of the content is set at 0.05 to 1.5%. 10038 [0077] Ni is an effective element in enhancing toughness and strength, and, to secure the effect, an addition amount of 0.05% or more is required. However, when the addition afficient exceeds 5%, weldability deteriorates, and therefore the upper limit is set at 5%.

| SEDE 0 | E000 0 | SEDE 0 | SED 2 ٤ b hardening, but a large amount of its addition exceeding 1:5% raises hardenability, generates a bainite structure and 2 deteriorates toughness. Therefore, the upper limits set at 1:5% 281 0.0 | e200.0 | 820.0 | 07.0 | 05.0 | 81.0 9 [0079] Mo is an element which enhances hardenability and at the same time, improves strength by forming carbonitrides. The addition amount of 0.02%, of more is required for securing the effect, but the addition in large amount (\* 8 exceeding 1.5% enhances strength excessively and deteriorates toughness considerably. Therefore, the range of the 0.1 0.09 0.22 1.48 0.002 0.0032 0.0041 0.034 0.0042 0.0022 content is set at 0.02 to 1.5%. 1.1 [0080] V is an element which forms carbides and nitrides and is effective in enhancing strength; but the effect cannot be 12 be secured with the addition amount of less than 0.01% and in contrast with this toughness deteriorates with the 13 61 addition amount; of exceeding 0.1%. Therefore, the range of the content is set at 0.01, to 0.1%. 1 82.0 83.0 21 [0081] Nb is an element which forms carbides and nitrides and is effective in enhancing strength, but the effect cannot ıί be secured with the addition amount of less than 0.0001% and toughness deteriorates with the addition amount of exceeding 0.2%. Therefore, the range of the content is set at 0.0001 to 0.2%. [0082] Each of Zr and Ta is like Nb, an element which forms carbides and nitrides and is effective in enhancing .3 strength, but the effect cannot be secured with the addition amount of less than 0.0001% and, in contrast with this, ではない toughness deteriorates with the addition amount of exceeding 0.05%. Therefore, the range of the content is set at 22 0.68 0.31 1.09 0.002 0.0039 0 0532 0:007 0.2059 0.0076 0.05 121-2 0.0001 to 0.05%. 22 [0083] B generally enhances hardeဂြိန်ပြုပြုနဲ့ which the state of solid solidition and list in the state of solid solidition and list in the state of solid solidition and list in the state of solid solidition and the state of solid soli 23 N in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solution by forming BN and entire to be in solid solutions. 24 be secured with the addition of 0.0003% or more; but its excessive addition causes the deterioration of toughness and 25 0.12 (0.25 1.11 0.065 in order 0.000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 2€ 95 [0084] Ca and REM suppress the generalion of elongated MnS by forming sulfides and improve the properties in the plate thickness direction of a steel material, particularly a lamellar tear property, Each of Ca and REM cannot secure the plate thickness direction of a steel material, particularly a lamellar tear property, Each of Ca and REM cannot secure the property. 5ء 95 29 those effects with the addition of less than 0,0005% and therefore the lower limit is set at 0,0005%. In contrast with arch QΣ this, with the addition exceeding 0.005%; the number of the oxides of Ca and REM increases and the number of ultra-15 fine Mg contained oxides decreases Therefore the upper limit is set at 0.005%. 1 500.0 | 50.0 | 50.0 | 61.0 ΞE 35 [0085] A steel containing above-mentioned components is refined in a steelmaking process, continuous casting, the ΞĒ DE heavy plate thus produced is heated and rolled: in this case, with regard to a rolling method, a heating and cooling method and a heat treatment method, even though methods conventionally applied in the relevant fields are adopted,

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there is no affection to HAZ toughness at all.

[0086] In particular, based on the fact that the smaller the grain size of a base steel is, the larger the grain size and the difference thereof at a HAZ are, the fining of a prior  $\gamma$  grain size at a HAZ according to the present invention demonstrates a large effect even in the case that not only HAZ toughness but also hardness matching, etc. have to be taken into consideration.

#### Examples

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[0087] Examples according to the present invention will be described hereunder.

[0088] Steel ingots having the chemical compositions shown in Tables 1 and 2 (continued from Table 1) were subjected to hot rolling and heat treatment and produced into steel plates, and thereafter the steel plates were welded with the small weld heat input of 1.7 kJ/mm, the large weld heat input of 20 kJ/mm and the ultra-large weld heat input of 150 kJ/mm. Then, prior γ grain sizes at HAZs were measured with the aforementioned cutting method and the susceptibility of HAZ toughness (test pieces were taken from the region of the coarsest grains) to heat inputs was evaluated by the Charpy impact test. The results are shown in Table 3.

[0089] Note that  $\Delta v \to 0$  in Table 3 is obtained by calculating the difference of Charpy absorbed energy between the cases of small heat input (1.7 kJ/mm) and ultra-large heat input (150 kJ/mm), that is, [toughness in case of small heat input: vEo (J)] - [toughness in case of ultra-large heat input: vEo (J)], and each absorbed energy is an average of the values obtained by the measurement of three test pieces at 0°C.

[0090] Further note that, with regard to \$1 and \$2, \$1 and \$2 are average particle intervals of oxides calculated from the photographs taken with an electron microscope in the magnification of 1,000 times for \$1 and 100,000 times for \$2.5 to be a local second of 1,000 times for \$1.000 times for \$2.5 to be a local second of 1,000 times

Table 1 (Continue to Table 2) (Table 2) Table 1 (Continue to Table 2) (Table 2) (Continue to Table 2) (Table 2)

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1	40,1	0.05	0.10	1.21	0.005	0.0030	0.0040	0.005	0.0033	0.0042	0.40	0.30	6. 30	1
2		0.15	0.13	1.32	0.008	0.0053	0.0030	0.003	0.0041	0.0008		l ra	1497	racou enr
3		0.10	0.08	1.50	0.003	0.0044	0.0084	0.012	0.0003	0.0032				•
4	∍alia.	0.14	0.07	1.60	0.004	0.0035	0.0005	0.016	0.0019	0.0025		ഭസ	i bobb	10073) Chia
5	\$142.5	0.15	0.25	(1447)	0:009	0.0053	0.0071	0.012	g0:0019'	00.0024	l .	nct-sc	0.15	hardannes, but
6		0.18	0.10	0.70	0.026	0.0029	0.0061	0.012	0.0025	0.0033	fore !	rectiff is	98 C.75	deleneration to
7	-coditi	0.19	0.02	0.31	0.003	0.0228	0.0053	0.013	0.0008	0.0028	មាន ជា	10.05	യികമ്	1 3 th [ 1.75 [ ]
8	र महरूत्	0.13	0.15	1 27	0.007	0.0051	0.0026	0.008	0.0028	0.0025	0.20	0.10	3 75 1	50 35T 200%
9	11/10	0.09	0.17	1.90	0.003	0.0002	0.0134	0.041	0.0098	0.0079	0.30	0.15	7	15 Yours Joseph
10	, ,	0.09	0.20	1.48	0.002	0.0032	0.0041	0.024	0.0042	0.0022	0.30	35, 1 2	50.0	e 7 e (91,000)
11	Invent-	0.11	0.25	1.35	0.004	0.0032	0.0051	0.012	0.0033	0.0035		1. ' "	0.15	
13	ed TONE	0.12	0.31	1.21	0.006	0.0105	0.0042	0.024	0.0041	0.0032	क्रिकेट करें हैं। इस्केट करें के स्ट्रिकेट के स्ट्र	Shart.		भवन (कारत
14	steel': %	0.13	0.09	1.35	0.006	0.0031	0.0008	0.013	0.0043	0.0005	140 T.E	1011.07	0.05	Principal and
15		0.06	0.28	1.05	0.004	0.0033	0.0061	0.012	60.0079.G	0.0078	6 125.	ಗತ್ತಿಕರ	0.25	เครียน เลยทอนเ
16	te anas	0.05	0.32	1121	0.003	0:0031	0.0058	0.008	0.0082 =	0.0052	10740	0:80	17,30	reich [F185]
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18		0.14	0.24	1.45	0.004	0.0053	0.0029	0.005	0.0028	0.0047	อกเลขาดก	l choic	0.10	าร.0 ฮูลเกอรเหล
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22	Anne	0.08:	0.31	1.20	0.004.	0.0025	0.0453	0.018	0.0054	0.0032	12204	<u> </u>	<del> </del>	146950) 13600)
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24 25	<u> </u>			2.40	0.015	0.0033	0.0008	0.013	0.0038		16.230	Schil		tiw ormaca ed
25	L	0.12	0.25	1.11	0.040	0.0045	0.0072	0.019	0.0031	0.0008	0.013	32 3 1	1	म वार्ग वार्याचा वर्ष
27		0.15	0.17	.0.95	0.003	.0.0351	0.0053	0.017	0.0005	0.0020				ľ
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29	ative	0.18	0.05	1.02	0.005	0.0031	0.0543	0.023	0.0083	0.0023	75183	2000	14.5 E.S.	and alleged and
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32		0.18	0.05	0.45	0.002	0.0015	0.0061	0.010	<0.0001	0.0009	sacus.	3C / SC	3.5 61	adres rateri
33	;	0.16	0.22	0.78	0.004	0.0081	0.0043	0.008	0.0228	0.0072	ر ا دور پیم		[	Lery E. Printers
34	276	0.05	0.41	1.79	0.003	0.0051	0.0052	0.045	0.0139	0-0090	0.10		0.14	Table General Section
35	#### <b>3</b> .	0.07	0.35	1.57	0.002	0.0035	0.0049	0.012	0.0119	0.0001	0:30	0.45	៩ខាខ្ម	कार कार्यालय द्वारक्षीत

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				Ta	ble 3 (d	continue	<b>d)</b> , ( , , , , , , , ,	TR & 2	nanca:	51 E 3	1.5			
			Production	Plate	d1	~ ~::d2	d3	· ∷λ1	: λ2	vEo	− ΔνΕο	}		
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Table 3. (co	ontinued)
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_				(mm)				(12)					
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large heat input. Though the steels 20-2 and 21-2 have almost the same chemical compositions as those of the steels

· 20 and 21, respectively, the deoxidizing conditions are varied and the Mg amounts are somewhat different. Though λ1 in case of the steel 20-2 and λ2 in case of the steel 21-2 are outside the range specified in the present invention, even in these cases, it is observed that the grain size of the steel 20-2 scarcely changes and it is understood that the grain size of the steel 21-2 is 200 µm or less at the heat input condition of 60.0 kJ/mm. Further, Charpy absorbed energy of all those invented steels exceeds 10 kgf-m and it shows that the above invented steels have high toughness. [0092] Moreover, the difference of Charpy absorbed energy between the cases of small heat input and ultra-large heat input is as small as 4 kgf-m at the largest and HAZ toughness does not vary even on the wide-ranging heat input conditions.

[0093] Note that there are cases where minus symbols are placed on the values of the aforementioned Charge 0.00. conditions. absorbed energy differences and that shows the toughness is improved in spite that the prior γ grain sizes become large. This results from the fact that the intragranular transformation ability of Mg contained oxides is extremely large, and this according to the present invention up to 100 to 100 is larger as the present inventions and the present inventions and the present inventions that the that [0094] On the other hand, the steels 23 to 35 are the comparative steels produced on other conditions than that specified in the present invention. More specifically, the comparative steels 23, 24, 25, 26, 27, 29, 30, 33, 34 and 35 are the comparative steels 23, 24, 25, 26, 27, 29, 30, 33, 34 and 35 are the cases where at least one of the basic components or the selective elements is added in the amount outside the composition range specified in the present invention. the composition range specified in the present invention.

[0095] In the aforementioned comparative steels, though the average grain intervals of oxides, which are an important requirement in the present invention, mostly satisfy the requirements specified in the present invention, elements causing toughness deterioration are added in excess and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and that results in accelerating the deterioration of HAZ toughness and the second of the second o when the steels are welded on small heat input conditions and ultra-large heat input conditions.

[0096] Comparative steels 28 and 31 are the cases where the amounts of Al and Ti are lower than their lower limits 20 specified in the present invention, respectively. In these cases, prior γ grain sizes coarsen as the heat input increases and thus the both comparative steels have poor toughness. [0097] Comparative steel 32 has no Mg addition, and under a small heat input condition, has good toughness. But under an ultra-large heat input condition, the steel has considerable deterioration of toughness and, consequently, the 25 large Charpy absorbed energy difference of 10.3 kgf-m. [0098] All of the comparative steels mentioned above have low HAZ toughness, and moreover the HAZ toughness further deteriorates when heat input amount is high. Zr. 0.0001 to 0.08% [0099] Comparative steels 33 and 34 have many fine oxides and, because of that, have largely deteriorated toughness even though the prior y grain sizes are sufficiently small compared with other cases. [0100] The reason is that coarse particles of 5 μm or more are mainly generated caused by the addition of an ex-P.C cessive amount of Mg or 0 and then brittle fracture is accelerated. cessive amount of Mg of 0 and then brittle fracture is accelerated.

[0101] Comparative steels 36 and 37 are the cases where their chemical compositions are the same as those of the invented steels 1 and 2, respectively, but the amounts of oxygen dissolved in molten steel exceed 50 ppm when the prescribed amounts of Mg are added at the final stage. [0102] After all, in comparative steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated sufficiently in the steel oxides are not generated at the steel oxides are not generated at the steel oxides are not generated at the steel oxides are not generated at the steel oxides are not generate 35 therefore the coarsening of prior  $\gamma$  grains and the considerable deterioration of toughness occur. A stest for a welded structure with HAZ couptiness: 1000 of the mediane according to any one of glaims, to In Construction of the prior sustant and the [0103] According to the chemical compositions and the production method specified in the present invention, the growth of prior, y grains, at a HAZ can be suppressed, while disregarding heat input conditions, by either adding a prescribed amount of Mg properly after adding Ti or adding a prescribed amount of Mg properly after adding Ti and Mg simultaneously.

[0104] In the present invention, it is possible to enhance HAZ toughness over wide-ranging heat input conditions by the supplied of the present invention. It is possible to enhance HAZ toughness over wide-ranging heat input conditions by the supplied of the present invention. It is possible to enhance HAZ toughness over wide-ranging heat input conditions by the supplied of the present invention. the suppression effect. [0105] As a result, in various technical fields including offshore structures, line pipes for transporting natural gas or crude oil, architecture, shipbuilding, bridges and construction equipment, safety against brittle fractures of welded structures is remarkably improved.

[0106] The present invention can, accordingly, greatly contribute to the development of various industrial technological provides an experience of the present invention can accordingly, greatly contribute to the development of various industrial technological provides and the present invention can accordingly greatly contribute to the development of various industrial technological provides and the present invention can accordingly greatly contribute to the development of various industrial technological provides and the present invention can accordingly greatly contribute to the development of various industrial technological provides and the present invention can accordingly greatly contribute to the development of various industrial technological provides and the present invention can accordingly greatly contribute to the development of various industrial technological provides and the present invention can accordingly greatly contribute to the development of various industrial technological provides and the present invention can be accordingly greatly contribute to the development of various industrial technological provides and the present invention can be accordingly greatly contribute to the development of various industrial technological provides and the present invention can be accordingly greatly as a provide and the present invention can be accordingly greatly as a provide and the present invention can be accordingly greatly as a provide and the present invention can be accordingly greatly as a provide and the present invention can be accordingly greatly as a provide and the present invention can be accordingly greatly as a provide and the present invention can be accordingly greatly as a provide and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present and the present a 38 gies. and and Mn at a stealmenting process or simultaneously affer carrying out a week provin-Leading Figure 10 at at 11 at 1 or casting the steel after fugher adding hitting a

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#### Claims

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1. A steel for a welded structure with HAZ toughness not susceptible to heat input, characterized by: containing, in terms of wt%,

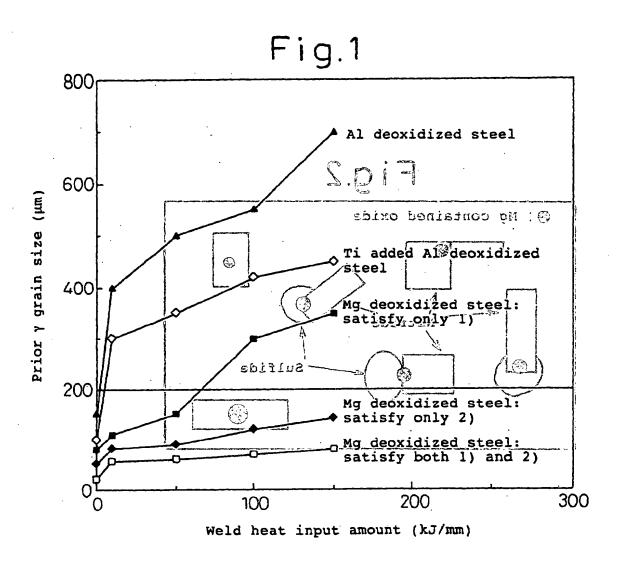
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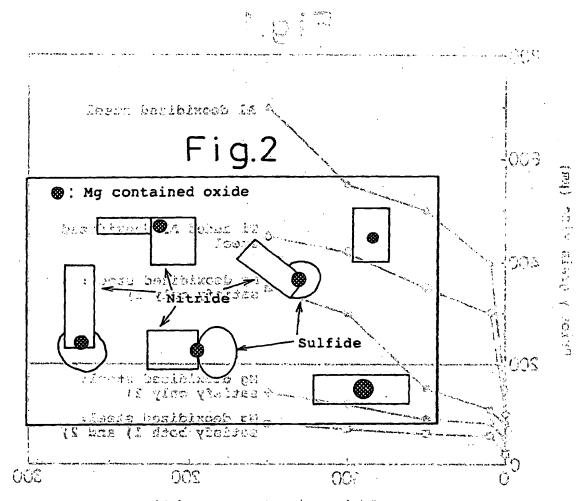
Tance reconsigned in noise tobactor subjectors will be a created to a grid sensor or a nigra-de-4. A steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of claims 1 to 3; characterized by having the prior austenite grain sizes of 10 to 200 µm in its HAZ structure without depending on weld heat input.

The same of the profit 40 5. A method for producing a steel for a welded structure with HAZ toughness insusceptible to heat input according to any one of claims 1 to 4, characterized by: casting the steel in the state of adjusting the dissolved oxygen amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and a required amount of Mg successively or simulations and the successively or simulations are successively or simulations and the successively or simulations are successively or simulations and the successively or simulations are successively or simulations and the successively or simulations are successively or simulations and the successively or simulations are successively or simulations are successively or simulations. taneously after carrying out a weak deoxidation treatment by adding Siland Mn at a steelmaking process; or casting 45 the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less.

10 489 Barrier grandes for segue on search and the segue of 6. A method for producing a steel for a welded structure with HAZ toughness insusceptible to heat input according ០០របាននូកខ to any one of claims 1 to 4, characterized by: casting the steel in the state of adjusting the dissolved oxygen [CT13] amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and required amounts of Al, Ca and Mg successively 50 or simultaneously after carrying out a weak deoxidation treatment by adding Si and Mn at a steelmaking process; or casting the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less. 0.13.19 55 The Control of the Historia of the market of the recent and the first of the Historia of the Control of the Co



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## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/07091

A. CLASS Int.	SIFICATION OF SUBJECT MATTER .Cl <sup>7</sup> C22C3B/00, C21C7/00										
According to	o International Patent Classification (IPC) or to both na	ational classification a	nd IPC								
	S SEARCHED										
Int.	Minimum documentation searched (classification system followed by classification symbols) Int.Cl <sup>7</sup> C22C38/00-38/60, 33/04, C21C7/00-7/06										
Jits Koka	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  Jitsuyo Shinan Koho 1926-1996 Jitsuyo Shinan Toroku Koho 1996-2000  Kokai Jitsuyo Shinan Koho 1971-2000 Toroku Jitsuyo Shinan Koho 1994-2000										
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI											
	MENTS CONSIDERED TO BE RELEVANT										
Category*	Citation of document, with indication, where ap			Relevant to claim No.							
P,X	JP, 11-293382, A (Nippon Steel 26 October, 1999 (26.10.99), Claims; column 4, lines 39-41	1-6									
х	JP, 9-310147, A (Nippon Steel C 02 December, 1997 (02.12.97), Claims (Family: none)		1-6								
х	JP, 10-298705, A (Nippon Steel 10 November, 1998 (10.11.98), Claims (Family: none)	•	1-6								
x	JP, 5-43977, A (Nippon Steel Co 23 February, 1993 (23.02.93), Claims (Family: none)	rporation),		1-6							
х	JP, 11-21613, A (Nippon Steel C 26 January, 1999 (26.01.99), Claims (Family: none)	orporation),		1-6							
Forther	r documents are listed in the continuation of Box C.	See patent fam.	· · · · · · · · · · · · · · · · · · ·								
	categories of cited documents:		published after the inter	metional filing date or							
"A" docume	categories of cites notements: ent defining the general state of the art which is not ared to be of particular relevance	priority date and		e application but cited to							
	ared to be of particular relevance document but published on or after the international filing	"X" document of part	nicular relevance; the c	criying the invention claimed invention cannot be red to involve an inventive							
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08 D	ectual completion of the international search December, 2000 (08.12.00)		he international sear ber, 2000 (1								
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Facsimile No	o	Telephone No.									

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